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(54) **PROCEDE DE PREPARATION D'UNE DISPERSION AQUEUSE  
DE POLYMERE**  
(54) **PREPARATION OF AN AQUEOUS POLYMER DISPERSION**

(57) Selon ce procédé de préparation d'une dispersion aqueuse de polymère, on prépare de façon connue en soi une dispersion aqueuse d'un polymère qui contient au moins un monomère chimiquement lié avec au moins un groupe éthyléniquement insaturé, de sorte que la teneur totale de la dispersion aqueuse de polymère en monomères libres, c'est-à-dire non chimiquement liés et pourvus d'au moins une liaison double éthyléniquement insaturée, soit supérieure à 0 et égale ou inférieure à 1 % en poids, par rapport à la teneur en polymère de la dispersion aqueuse de polymère. Cette teneur résiduelle en monomères est ensuite réduite au moyen d'un système initiateur d'oxydoréduction radicalaire qui comprend au moins un agent oxydant et au moins un agent réducteur. Le système initiateur d'oxydoréduction contient comme agent réducteur un mercaptane qui contient, en plus du groupe mercaptane, au moins un autre groupe fonctionnel.

(57) In this process for preparing an aqueous polymer dispersion, an aqueous dispersion of a polymer that contains at least one chemically bound monomer having at least one ethylenically unsaturated group is prepared in a manner known per se, so that the total content of free, i.e. non chemically bound, monomers that contain at least one ethylenically unsaturated double bond, in the thus prepared aqueous polymer dispersion, lies in a range from > 0 to < 1 % by weight, with respect to the polymer content of the aqueous polymer dispersion. This residual monomer content is then reduced by means of a radical redox initiator system that includes at least one oxidising agent and at least one reducing agent. The redox initiator system contains as reducing agent a mercaptane with at least one other functional group besides the mercaptane group.



**PCT**  
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(54) Title: PROCESS FOR PREPARING AN AQUEOUS POLYMER DISPERSION (54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG EINER WÄSSRIGEN POLYMERISATDISPERSION (57) Abstract <p>In this process for preparing an aqueous polymer dispersion, an aqueous dispersion of a polymer that contains at least one chemically bound monomer having at least one ethylenically unsaturated group is prepared in a manner known per se, so that the total content of free, i.e. non chemically bound, monomers that contain at least one ethylenically unsaturated double bond, in the thus prepared aqueous polymer dispersion, lies in a range from &gt; 0 to ≤ 1 % by weight, with respect to the polymer content of the aqueous polymer dispersion. This residual monomer content is then reduced by means of a radical redox initiator system that includes at least one oxidising agent and at least one reducing agent. The redox initiator system contains as reducing agent a mercaptane with at least one other functional group besides the mercaptane group.</p> (57) Zusammenfassung <p>Ein Verfahren zur Herstellung einer wässrigen Polymerisatdispersion, bei dem man eine wässrige Dispersion eines Polymerisats, das wenigstens ein wenigstens eine ethylenisch ungesättigte Gruppe aufweisendes Monomeres in chemisch gebundener Form eingebaut enthält, in an sich bekannter Weise so erzeugt, daß der Gesamtgehalt der wässrigen Polymerisatdispersion an freien, d.h. nicht chemisch gebundenen, wenigstens eine ethylenisch ungesättigte Doppelbindung aufweisenden Monomeren, bezogen auf den Polymerisatgehalt der wässrigen Polymerisatdispersion, im Bereich von &gt; 0 bis ≤ 1 Gew.-% liegt und anschließend diesen Restmonomeregehalt durch Einwirkung eines wenigstens ein Oxidationsmittel und wenigstens ein Reduktionsmittel umfassenden radikalischen Redoxinitiatorsystems verringert, wobei das Redoxinitiatorsystem als Reduktionsmittel ein Mercaptan umfaßt, das neben der Mercaptangruppe wenigstens eine weitere funktionelle Gruppe aufweist.</p>		

### Preparation of an aqueous polymer dispersion

The present invention relates to a process for the preparation of an aqueous polymer dispersion, in which an aqueous dispersion of a polymer which contains at least one monomer, having at least one ethylenically unsaturated group, incorporated in chemically bonded form is produced in a manner known per se, so that the total content, based on the polymer content of the aqueous polymer dispersion, of monomers which are free, i.e. not chemically bonded, and have at least one ethylenically unsaturated double bond (referred to in this publication as residual monomer content) is from  $> 0$  to  $\leq 1\%$  by weight, and this residual monomer content is then reduced by the action of a free radical redox initiator system comprising at least one oxidizing agent and at least one reducing agent.

Aqueous polymer dispersions are fluid systems which contain polymer particles as a stable disperse phase in an aqueous dispersing medium. The diameter of the polymer particles is in general mainly from  $0.01$  to  $5\ \mu\text{m}$ , frequently mainly from  $0.01$  to  $1\ \mu\text{m}$ . The stability of the disperse phase often extends over a period of  $\geq 1$  month, often even over a period of  $\geq 3$  months. Its polymer volume content is usually from  $10$  to  $70\%$  by volume, based on the total volume of the aqueous polymer dispersion.

As in the case of polymer solutions on evaporation of the solvent, aqueous polymer dispersions have the property of forming polymer films on evaporation of the aqueous dispersing medium, and aqueous polymer dispersions are therefore widely used as binders, for example for surface coating materials or materials for coating leather.

In principle, a person skilled in the art classifies aqueous polymer dispersions as aqueous secondary dispersions and aqueous primary dispersions. The aqueous secondary dispersions are those in the preparation of which the polymer is produced outside the aqueous dispersing medium, for example in solution in a suitable nonaqueous solvent. This solution is then transferred to the aqueous dispersing medium and the solvent is separated off, as a rule by distillation, with dispersing. In contrast, aqueous primary dispersions are those in which the polymer is produced directly as the disperse phase in the aqueous dispersing medium itself. The common feature of all preparation processes is essentially that monomers which have at least one ethylenically unsaturated group are concomitantly used for the synthesis of the

polymer, or that said synthesis is effected exclusively from such monomers.

Such monomers having at least one ethylenically unsaturated group  
5 are usually incorporated by initiated polymerization reaction,  
the type of initiation used being determined in particular by the  
desired performance characteristics of the end product and there-  
fore being adapted to these. For example, ionic or free radical  
initiation is suitable. However, the incorporation may also be  
10 effected by catalytically initiated polymer-analogous reaction.  
Free radical initiation is particularly frequently used, and  
hence the one or more monomers having at least one ethylenically  
unsaturated group are incorporated as a rule by the free radical  
aqueous emulsion polymerization method in the case of aqueous  
15 primary dispersions and as a rule by the free radical solution  
polymerization method in the case of aqueous secondary disper-  
sions.

Since, taking into account the periods required for this purpose,  
20 it is as a rule not practical to strive for a complete conversion  
with regard to the incorporation of the one or more monomers hav-  
ing at least one ethylenically unsaturated group, maintaining the  
actual polymerization reaction conditions determining the desired  
properties (for example molecular weight, molecular weight dis-  
25 tribution, degree of branching, etc.) of the end product, the  
aqueous polymer dispersions resulting after the end of this main  
polymerization reaction usually contain free monomers which are  
not chemically bonded in the dispersed polymer and have at least  
one ethylenically unsaturated double bond. Owing to the increased  
30 reactivity of the ethylenically unsaturated double bond, such re-  
sidual monomers, eg. acrylonitrile and vinyl acetate, are not  
toxicologically completely safe and are therefore undesirable  
from both the manufacturer's and the consumer's point of view.

35 A very wide range of methods are already available for reducing  
the residual monomer content of aqueous polymer dispersions.

EP-A 584 458 discloses the reduction of the residual monomer  
content of aqueous polymer dispersions by stripping by means of  
40 steam. EP-B 327 006 recommends the use of conventional  
distillation.

These processes are disadvantageous in that, although they are  
capable of reducing the residual monomer content of the aqueous  
45 polymer dispersion, they do not deal with the disposal of the re-  
sidual monomers. The latter problem is merely shifted to another  
level. Moreover, their use is generally accompanied by changes in

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the solids content of the aqueous polymer dispersion and adverse effects on the stability of the disperse phase.

EP-A 505 959 relates to a process for reducing the content of vinyl acetate in aqueous polyvinyl acetate dispersions. According to the process of EP-A 505 959, the monomeric vinyl acetate still remaining is hydrolyzed in a weakly alkaline medium to give acetic acid and acetaldehyde, the latter being oxidized to acetic acid by added hydrogen peroxide. However, the disadvantage of this procedure is that, owing to an additional electrolyte load, it adversely affects the stability of the aqueous polymer dispersion and causes emissions of acetic acid.

DE-A 42 10 208 relates to a process for reducing the content of free vinyl acetate and vinyl propionate in aqueous polymer dispersions. The process essentially corresponds to a combined use of stripping and hydrolysis of these monomers, and the disadvantages of the abovementioned procedures therefore also apply to the process of DE-A 42 10 208.

DE-A 30 06 172 relates to a process for reducing the content of free acrylonitrile in aqueous polymer dispersions. In this procedure, additional monomers which are characterized by a pronounced tendency toward free radical copolymerization with acrylonitrile are added to the aqueous polymer dispersion, and the free radical main polymerization reaction is continued.

DE-A 38 34 734, EP-A 379 892 and EP-A 327 006 disclose that the content of residual monomers in aqueous polymer dispersions can be reduced by free radical postpolymerization after the end of the main polymerization reaction, which postpolymerization is effected by the action of particular free radical redox initiator systems which, for various reasons, are frequently less suitable for the main polymerization. Such redox initiator systems comprise at least one oxidizing agent, at least one reducing agent and, if required, one or more transition metal ions occurring in different valency states. The reducing agent plays a key role with regard to the postpolymerization efficiency of the free radical redox initiator system in aqueous polymer dispersions.

It should in particular be such that when it is used in a redox initiator system for free radical postpolymerization in aqueous polymer dispersions

- an effective reduction of the amount of residual monomers is achieved without the stability of the aqueous polymer dispersion being substantially impaired,
  - 5 - the redox initiator system displays its advantageous effect also at a pH of the aqueous dispersing medium of from  $\geq 6$  to 10, preferably from 7 to 9, since the vast majority of all aqueous polymer dispersions are anionically stabilized,
  - 10 - the presence of a transition metal ion is not essential, since the latter remain in the aqueous polymer dispersion after the end of the postpolymerization,
  - essentially no discoloration of the films of the aqueous  
15 polymer dispersion results and
  - as far as possible no volatile organic secondary products are produced.
- 20 Particularly taking into account the last-mentioned point of view, one requirement which the reducing agent has to meet is that it be capable of displaying its effectiveness also in combination with an inorganic oxidizing agent. Thus, organic oxidizing agents, for example organic peroxides or hydroperoxides, usually result in the formation of volatile organic secondary products, which are undesirable both from the point of view of the producer of the aqueous polymer dispersion and from the point of view of the user of the aqueous polymer dispersion (eg.  $R-O-O-H \rightarrow R-OH$ ).
- 30 US-A 4 529 753, columns 3 and 4, recommends reducing sugars and acid derivatives thereof, eg. ascorbic acid, and alkali metal disulfite as reducing agents suitable in free radical redox initiator systems for free radical postpolymerization in aqueous  
35 polymer dispersions, sodium metabisulfite being singled out as being a particularly suitable reducing agent. EP-B 327 006, page 7, confirms this recommendation in US-A 4 529 753 and mentions sulfoxylates, such as the sodium salt of hydroxymethanesulfinic acid (Rongalit®C), as further correspondingly suitable reducing  
40 agents. A redox initiator system comprising Rongalit C is also used in Example 1 of EP-A 379 892 and in DE-A 38 34 734 for free radical postpolymerization in an aqueous polymer dispersion.

However, the disadvantage of these reducing agents recommended in  
45 the prior art is that they do not fully meet the requirements described above.

Thus, the use of ascorbic acid as a reducing agent results in discolored films of the aqueous polymer dispersion. Alkali metal metabisulfite does not sufficiently effectively reduce the amount of residual monomers, and readily volatile formaldehyde is liberated when hydroxymethanesulfinic acid is used.

US-A 4 529 753 recommends the simultaneous use of postpolymerization and stripping with steam, and this recommendation therefore also has the disadvantages described above.

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Furthermore, it is usually possible to achieve residual monomer contents of 1 % by weight or less, based on the polymer content of the aqueous polymer dispersion, when the prior art processes for reducing the residual monomer content of aqueous polymer dispersions are used, but increasing difficulties in reducing the residual monomer content are encountered below the 1 % by weight limit. These difficulties are presumably due to the fact that the residual monomers in an aqueous polymer dispersion may be present both on the dispersed polymer particles and in the aqueous dispersing medium. A distribution equilibrium is established between these two phases. The disadvantage of the known methods for reducing the residual monomer content of aqueous polymer dispersions appears to be based on the fact that they cover essentially either only the aqueous dispersing medium or only the polymer particles, ie. a significant total reduction of the residual monomer content of the aqueous polymer dispersion takes place in an essentially diffusion-controlled manner (repeated establishment of the distribution equilibrium), which is presumably the reason for the unsatisfactory rate of reduction of the residual monomer content in aqueous polymer dispersions when the known methods are used.

Accordingly, DE-A 39 09 790, which relates to processes for eliminating unsaturated compounds capable of free radical polymerization from aqueous systems other than aqueous polymer dispersions, also gives no indication of an efficient reduction of the residual monomer content of aqueous polymer dispersions.

The possibility of distribution over two different phases is presumably also a reason why the reduction of the residual monomer content in aqueous polymer dispersions by the prior art processes in the case of a residual monomer mixture which comprises at least two monomers A and B which differ from one another and whose difference generally also results in different solubilities thereof both in the aqueous dispersing medium and in the dis-

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persed polymer particles does not take place uniformly for the residual monomers which differ from one another.

The prior applications DE-A 44 19 518 and DE-A 44 35 423 recommend the use of free radical redox initiator systems which contain the adduct of a ketone with the bisulfite anion as reducing agent for the uniform reduction of contents of residual monomers which differ from one another. However, the disadvantage of these reducing agents is that the ketone is generally liberated when they are used. Furthermore, they display their action in particular in combination with organic peroxides.

The prior application DE-A 44 35 422 recommends the use of amino-iminomethanesulfinic acid (formamidinesulfinic acid) as a reducing agent in free radical redox initiator systems for eliminating the residual monomers in aqueous polymer dispersions. However, the disadvantage of this reducing agent is its limited solubility in water, i.e. it must be added either as a solid or as a very dilute aqueous solution to the aqueous polymer dispersion containing the residual monomers. Both are disadvantageous when used on an industrial scale.

It is an object of the present invention to provide a process for reducing the residual monomer content of an aqueous polymer dispersion by the action of a free radical redox initiator system comprising at least one oxidizing agent and at least one reducing agent, which process does not have the disadvantages of the known processes for reducing residual monomer contents in aqueous polymer dispersions.

We have found that this object is achieved by a process for reducing the residual monomer content of an aqueous polymer dispersion, in which an aqueous dispersion of a polymer which contains at least one monomer, having at least one ethylenically unsaturated group, incorporated in chemically bonded form is produced in a manner known per se, so that the total content, based on the polymer content of the aqueous polymer dispersion, of monomers which are free, i.e. not chemically bonded, and have at least one ethylenically unsaturated double bond is from  $> 0$  to  $\leq 1\%$  by weight, and this residual monomer content is then reduced by the action of a free radical redox initiator system comprising at least one oxidizing agent and at least one reducing agent, wherein the redox initiator system contains, as reducing agent, at least one mercaptan which, in addition to the mercapto(thiol) group, has at least one further functional group which comprises at least one atom (preferably at least one atom selected from the group consisting of P, O, N, S, F, Cl, Br and I) other than



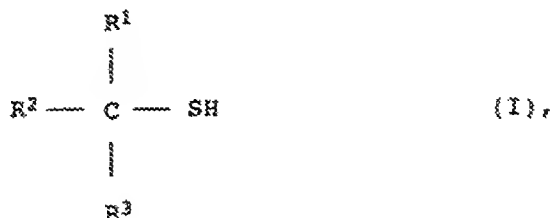
hydrogen and carbon and whose electronegativity is above that of the hydrogen atom (cf. H. R. Christen, Grundlagen der allgemeinen und anorganischen Chemie, Sauerländer Verlag Aarau, page 72 (1973)), with the exclusion of those processes in which the total amount of mercaptan is added completely to the aqueous polymer dispersion containing residual monomers before the addition of the oxidative component of the free radical redox initiator system.

10 The novel process can of course also be used for residual monomer contents of from  $10^{-3}$  to 0.5 % by weight or from  $10^{-3}$  to 0.1 % by weight, based on the polymer content of the aqueous polymer dispersion.

15 Processes in which an oxidative free radical initiator is added to an aqueous polymer dispersion which contains residual monomers and already contains added mercaptan are generally known (cf. for example US-A 3 833 550 and DE-A 23 54 681). However, the primary object of these processes is not a reduction of the residual  
20 monomer content but a reduction of the content of mercaptan which had been added during the preparation of the aqueous polymer dispersion for regulating the molecular weight of the polymer. It is on the one hand this regulating action which distinguishes the reducing agents to be used according to the invention from the  
25 prior art reducing agents and ensures that the reducing agents to be used according to the invention are very probably bound in sparingly volatile form in the course of the reduction of the residual monomer content.

30 Preferred mercaptans to be used according to the invention are mercaptans selected from the group consisting of thiocarboxylic acids of 1 to 8 carbon atoms and the alkali metal and ammonium salts thereof and the members which differ from thiocarboxylic acids of 1 to 8 carbon atoms and are of the general formula I

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where  $R^1$ ,  $R^2$ ,  $R^3$ , independently of one another, are each hydrogen,  
45 one of the following functional groups  $-OR^4$  where  $R^4$  is hydrogen or  $C_1$ - $C_4$ -alkyl,  $-NHR^4$ ,  $-COOR^4$ ,  $-SO_2R^4$ ,  $-SO_3R^4$ ,  $-OSO_3R^4$ ,  $-SR^4$ ,  $-NO_2$ ,  $-CN$ ,  $-SCN$ ,  $-halide$ ,  $-COSR^4$ ,  $-CSOR^4$ ,  $-COR^4$ ,  $-CSR^4$ ,  $-CSSR^4$ ,  $-CSNHR^4$ ,

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-CONHR<sup>4</sup>, -COOhalide, -CSShalide where halide is F, Cl, Br or I, -OPO<sub>3</sub>HR<sup>4</sup>, -PO<sub>3</sub>HR<sup>4</sup> and -OPO<sub>2</sub>R<sup>4</sup>, the alkali metal and ammonium salt thereof also being suitable in the case of acidic functional groups, a phenyl radical, a benzyl radical or an alkyl radical of 1 to 8 (preferably 1 to 4) carbon atoms, where one or two hydrogen atoms of each of these radicals may be replaced by one of the above functional groups and where two of the unsubstituted or substituted alkyl radicals may furthermore form a saturated ring having 5 or 6 carbon atoms, with the proviso that the compounds I have at least one and not more than three of the abovementioned functional groups in addition to the thiol group, and at least one of the radicals R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is an unsubstituted or substituted phenyl or benzyl radical or an unsubstituted or substituted alkyl radical of 1 to 8 (preferably 1 to 4) carbon atoms, as described above.

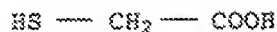
The particularly advantageous results obtained when the abovementioned reducing agents are used according to the invention are probably attributable, inter alia, to the fact that these mercaptans on the one hand have a certain water solubility (as a rule the solubility at 1 bar and 25°C is  $\geq 1$  % by weight, based on water; mercaptans to be used according to the invention and having such solubility behavior in water are generally preferred), but on the other hand are also capable of penetrating the fairly lipophilic polymer particles.

Further advantageous mercaptans to be used according to the invention are those such as mercaptobenzoic acid, mercaptoacetic acid and mercaptoethanol.

Particularly suitable according to the invention are those compounds I in which additionally at least one of the radicals R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is hydrogen. Other preferred compounds I are those which, in addition to the thiol group, have only one or two of the abovementioned functional groups, among which carboxyl, amino and sulfo are preferred.

Advantageous mercaptans to be used according to the invention are

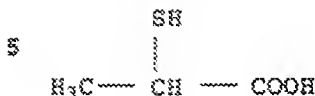
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mercaptoacetic acid,



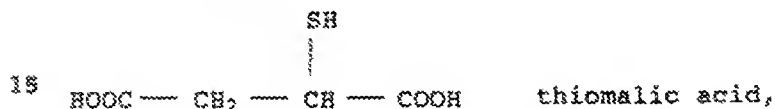
3-mercaptopropionic acid,



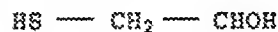
2-mercaptopropionic acid,



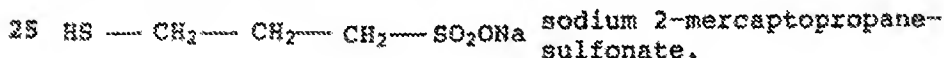
thioacetic acid,



thiomalic acid,

L-cysteine  
({R)-2-amino-3-mercaptopropionic acid),

mercaptoethanol,

sodium 2-mercaptopethanesulfonate  
andsodium 2-mercaptopropane-  
sulfonate.

At this point, it should be stated once again that the nature of the polymer dispersed in the aqueous medium plays essentially no role with regard to the success of the novel process, i.e. the term polymer comprises here polycondensates, such as polyesters, as well as polyadducts, such as polyurethanes, and polymers which are obtainable by ionic or free radical polymerization of exclusively monomers having at least one ethylenically unsaturated double bond, and mixed variants of the stated types. All that is important here is that at least one monomer having at least one ethylenically unsaturated group is involved in the synthesis of the polymer dispersed in the aqueous medium, so that there can be no problem at all with regard to the removal of residual monomers. The method of incorporation of the one or more monomers having at least one ethylenically unsaturated double bond into the dispersed polymer is unimportant according to the invention. It may be effected directly by means of ionic or free radical polymerization, by polymer-analogous reactions or by direct polyaddition or polycondensation. It should also be stated that the terminology aqueous polymer dispersion without further

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qualification in this publication covers both aqueous primary and aqueous secondary dispersions.

The preparation of aqueous polymer dispersions of the abovementioned different polymer types has been described before in many publications and is therefore sufficiently well known to a person skilled in the art (cf. for example Encyclopedia of Polymer Science and Engineering, Vol. 8, page 659 et seq. (1987); D.C. Blackley, in High Polymer Latices, Vol. 1, page 35 et seq. (1966); H. Warson, The Applications of Synthetic Resin Emulsions, page 246 et seq., chapter 5 (1972); D. Diederich, Chemie in unserer Zeit 24 (1990), 135-142; Emulsion Polymerization, Interscience Publishers, New York (1965); DE-A 40 03 422 and Dispersionen synthetischer Hochpolymerer, F. Hölscher, Springer-Verlag, Berlin (1969)).

Monomers having at least one ethylenically unsaturated group which are suitable for the novel process include in particular monomers which can be subjected to free radical polymerization in a simple manner, such as the olefins, eg. ethylene, vinylaromatic monomers, such as styrene,  $\alpha$ -methylstyrene, o-chlorostyrene or vinyltoluenes, esters of vinyl alcohol and monocarboxylic acids of 1 to 18 carbon atoms, such as vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl laurate, vinyl pivalate and vinyl stearate, and commercially available monomers VEOVA® 9-11 (VEOVA X is a trade name of Shell and stands for vinyl esters of carboxylic acids, which are also referred to as Versatic® X acids), esters of  $\alpha,\beta$ -monoethylenically unsaturated mono- and dicarboxylic acids of, preferably, 3 to 6 carbon atoms, in particular acrylic acid, methacrylic acid, maleic acid, fumaric acid and itaconic acid, with alkanols of, in general, 1 to 12, preferably 1 to 8, in particular 1 to 4, carbon atoms, especially methyl, ethyl, n-butyl, isobutyl, tert-butyl and 2-ethylhexyl acrylate and methacrylate, dimethyl maleate and n-butyl maleate, nitriles of  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acids, such as acrylonitrile, and conjugated C<sub>4</sub>-C<sub>8</sub>-dienes, such as 1,3-butadiene and isoprene. In the case of aqueous polymer dispersions produced exclusively by the free radical aqueous emulsion polymerization method, the stated monomers are as a rule the main monomers, which together usually account for more than 50 % by weight, based on the total amount of the monomers to be polymerized by the free radical aqueous emulsion polymerization method. As a rule, these monomers have only moderate to low solubility in water under standard conditions (25°C, 1 bar).

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Monomers which have higher water solubility under the abovementioned conditions are, for example,  $\alpha,\beta$ -monoethylenically unsaturated mono- and dicarboxylic acids and amides thereof, eg. acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, acrylamide and methacrylamide, and vinylsulfonic acid and the water-soluble salts thereof and N-vinylpyrrolidone.

In the case of aqueous polymer dispersions produced exclusively by the free radical aqueous emulsion polymerization method, the abovementioned monomers having high water solubility are usually copolymerized only as modifying monomers in amounts of less than 50, as a rule from 0.5 to 20, preferably from 1 to 10, % by weight, based on the total amount of the monomers to be polymerized.

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Monomers which usually increase the internal strength of the films of the aqueous polymer dispersions usually have at least one epoxy, hydroxyl, N-methylol or carbonyl group or at least two nonconjugated ethylenically unsaturated double bonds. Examples of these are N-alkylolamides of  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acids of 3 to 10 carbon atoms and esters thereof with alkenols of 1 to 4 carbon atoms, among which N-methylolacrylamide and N-methylolmethacrylamide are very particularly preferred, monomers having two vinyl radicals, monomers having two vinylidene radicals and monomers having two alkenyl radicals. Particularly advantageous are the diesters of dihydric alcohols with  $\alpha,\beta$ -monoethylenically unsaturated monocarboxylic acids, among which acrylic and methacrylic acid are preferred. Examples of such monomers having two nonconjugated ethylenically unsaturated double bonds are alkylene glycol diacrylates and dimethacrylates, such as ethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylates and propylene glycol diacrylate, divinylbenzene, vinyl methacrylate, vinyl acrylate, allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, methylenebisacrylamide, cyclopentadienyl acrylate or triallyl cyanurate. Also of particular importance in this context are the  $C_1$ - $C_8$ -hydroxyalkyl esters of methacrylic and acrylic acid, such as n-hydroxyethyl, n-hydroxypropyl or n-hydroxybutyl acrylate and methacrylate, and compounds such as diacetoneacrylamide and acetylacetoxyethyl acrylate and methacrylate, ureidoethyl methacrylate and acrylamidoglycolic acid. In the case of aqueous polymer dispersions produced exclusively by the free radical aqueous emulsion polymerization method, the abovementioned monomers are generally copolymerized in amounts of from 0.5 to 10 % by weight, based on the total amount of the monomers to be polymerized.

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The advantage of the uniform reduction of the monomer content by the novel process is displayed in particular when the residual monomers to be eliminated comprise two or more than two monomers which differ from one another and have at least one ethylenically unsaturated group, ie. the use of the process proves advantageous when three or four or five or six or more residual monomers which differ from one another are present in the aqueous polymer dispersion to be treated according to the invention.

10 This is true especially when the residual monomers contained in the aqueous polymer dispersion are such that they have molar solubilities  $S$  in 1000 g of water (= molal solubility in water) which differ significantly from one another under the postpolymerization conditions (as a rule, these solubilities are essentially very similar to those at 25°C and 1 bar).

If, in a residual monomer mixture, the residual monomer which has the highest molal solubility  $S_A$  is denoted by A and the residual monomer which has the lowest molal solubility  $S_B$  is denoted by B, the success according to the invention is achieved essentially independently of whether the ratio  $S_A/S_B$  has a value of  $\geq 1.1$  or  $\geq 1.5$  or  $\geq 2$  or  $\geq 5$  or  $\geq 10$  or  $\geq 50$  or  $\geq 100$  or  $\geq 1000$  or  $\geq 100,000$ .

25 In other words, the success according to the invention is achieved as a rule if the residual monomers contain at least one residual monomer which was assigned in the above list of possible residual monomers to the group comprising the monomers having moderate to low solubility in water, and at least one residual monomer which was assigned in the corresponding list to the group having high water solubility.

An advantage of the novel process is that the reducing agents to be used according to the invention result in essentially no secondary products which adversely affect the quality (in particular stability) of aqueous polymer dispersions. This makes it possible simultaneously to use the novel process and stripping processes which set high requirements with regard to stability, ie. directly to couple chemical and physical reduction of the residual monomer content, as recommended in US-A 4 529 753. Furthermore, this state of affairs forms the basis for using the novel process, for example in contrast to elimination of the residual monomers by stripping by means of steam, without difficulties, essentially independently of the solids volume content (solids volume, based on the volume of the aqueous polymer dispersion), ie. the solids volume content may be from 10 to 50 or from 20 to 60 or from 30 to 70 % by volume, as is the case, for example, in

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the aqueous polymer dispersions of DE-A 42 13 965, the applicability at high solids volume concentration (from 50 to 70 % by volume or higher) being of particular interest.

- 5 Another advantage is that the novel process can be used both in alkaline and in acidic aqueous dispersing medium, ie. the range of use extends from pH 1 to 12.

The applicability at acidic pH is important, for example, when  
10 the aqueous polymer dispersion contains from  $\geq 5$  to 60 % by weight, based on the polymer, of acrylic acid as copolymerized units. If the pH of aqueous dispersions of polymers having the abovementioned acrylic acid content is increased, the dynamic viscosity thereof increases considerably. Such aqueous polymer  
15 dispersions are therefore advantageously used as thickener dispersions (cf. for example German Patents 1,164,095, 1,264,945, 1,258,721, 1,546,315 and 1,265,752). In this context, they are produced in an acidic medium with relatively low viscosity. The thickening effect is not achieved until the user increases the  
20 pH. This is one of the cases where the reduction in the residual monomer content is to be carried out by the manufacturer of the aqueous polymer dispersion at a pH of the aqueous dispersing medium of less than 7 (as a rule from  $< 7$  to 2).

- 25 However, the novel process is preferably used at a pH of the aqueous dispersing medium of from 6 to 10, particularly preferably from 7 to 9. This is advantageous for those aqueous polymer dispersions whose disperse phase is stabilized by the presence of anionic groups. These are, for example, aqueous polymer disper-  
30 sions which are stabilized by the presence of anionic emulsifiers or which contain  $\alpha, \beta$ -monoethylenically unsaturated carboxylic acids of 3 to 6 carbon atoms, such as acrylic acid, as polymerized units (as a rule from 0.1 to 5, preferably from 0.5 to 4, % by weight, based on the dispersed polymer) in order to stabilize  
35 the disperse phase alone or concomitantly.

Remarkably, it is not necessary, in the case of the novel reduction of the residual monomer content (even at application temperatures of from 20 to 60°C), to use the novel redox initiator system in the presence of a metal compound which is soluble in the  
40 aqueous reaction medium and whose metallic component (eg. iron, vanadium or a mixture thereof) may occur in a plurality of valency states. However, a use in the presence of such a compound is of course also possible. As a rule, the amounts then used are  
45 from 0.01 to 1 % by weight, based on oxidizing or reducing agent (the respective component present in less than stoichiometric amount) and calculated as metal compound to be added. Examples of



suitable compounds of this type are iron(II) sulfate, iron(II) chloride, iron(II) nitrate, iron(II) acetate and the corresponding iron(III) salts, ammonium or alkali metal vanadates (V(V)), vanadium(III) chloride, vanadyl(V) trichloride and in particular vanadyl(IV) sulfate pentahydrate. Complexing agents (eg. EDTA) which keep the metals in solution under the reaction conditions are frequently also added.

With regard to the temperatures to be used in the novel reduction of the residual monomer content, the range from 0 to 100°C, preferably from 20 to 90°C, particularly 60 to 80°C, is recommended. However, correspondingly higher temperatures are also possible under superatmospheric pressure. A suitable working pressure is from  $\geq 1$  bar to 15 bar. It is particularly advantageous to carry out the novel postpolymerization at above the minimum film formation temperature, MFT (white point temperature), of the resulting aqueous polymer dispersion. In the case of aqueous polymer dispersions whose MFT is below 0°C, the static glass transition temperature  $T_g$  (DSC, midpoint temperature) of the dispersed polymer (cf. Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, Vol. A21 (1992), page 169) replaces the MFT. The working temperature is preferably at least 20°C, particularly preferably at least 40°C, more advantageously at least 60°C, very particularly preferably at least 80°C, very particularly advantageously at least 100°C above the relevant MFT or  $T_g$  (this relationship should be valid generally for postpolymerizations). In the case of polymer dispersions which have more than one  $T_g$ , the lowest of these values is to be used.

As for the free radical polymerization method generally, the process according to the invention can be used both under an inert gas atmosphere (eg.  $N_2$  or Ar) and under an oxygen-containing atmosphere (eg. air).

The fact that the use of the novel process usually gives rise to no discoloration of the resulting aqueous polymer dispersions is also advantageous. Other advantages are the excellent handling properties and shelf life of the reducing agents to be used according to the invention.

40

As stated above, the novel process can be applied in particular to those aqueous polymer dispersions whose dispersed polymer is produced by the free radical aqueous emulsion polymerization method from monomers having at least one ethylenically unsaturated group, with the exception of the novel elimination of residual monomers, and all statements made in this publication therefore relate in particular to those aqueous primary dispersions

## 15

prepared by the free radical aqueous emulsion polymerization method. The free radical aqueous emulsion polymerization is preferably carried out by the feed method, ie. the predominant amount of the monomers to be polymerized, as a rule from 50 to 5 100, preferably from 70 to 100, particularly preferably from 80 to 100, very particularly advantageously from 90 to 100, % by weight of their total amount, are added to the polymerization vessel only at the beginning of the free radical aqueous emulsion polymerization, according to the progress of the polymerization 10 of the monomers already present in the polymerization vessel. As a rule the addition is effected by continuous feed (generally in the form of pure monomer feed or preemulsified in the aqueous phase), in a manner such that at least 80, preferably at least 90, very particularly preferably at least 95, % by weight of the 15 monomers already present in the polymerization vessel have been incorporated as polymerized units. Aqueous seed polymer dispersions may be present for establishing the particle size of the dispersed polymer particles (cf. EP-B 40419 and Encyclopedia of Polymer Science and Technology, Vol. 5, John Wiley & Sons Inc., 20 New York (1966), page 847).

Suitable free radical polymerization initiators for the main polymerization reaction described above are all those which are capable of initiating a free radical aqueous emulsion polymeriza- 25 tion. These are both peroxides and azo compounds. However, redox initiator systems are of course also suitable. As a rule, the free radical initiator system used for the main polymerization will differ from the free radical initiator system to be used according to the invention for the postpolymerization. Furthermore, 30 as a rule at least 50, more frequently at least 75, generally at least 90, % by weight of the monomers to be polymerized in the main polymerization are polymerized in the absence of the novel reducing agent, ie. the main polymerization usually comprises no novel reducing agent. The use of peroxodisulfuric acid and/or the 35 alkali metal salts thereof and/or its ammonium salt as free radical initiator is preferred for carrying out the free radical aqueous emulsion polymerization particularly efficiently as the main polymerization reaction from the point of view of the desired properties and with respect to high cost-efficiency. The 40 amount of free radical initiator systems used is preferably from 0.1 to 2 % by weight, based on the total amount of the monomers to be polymerized. The manner in which the free radical initiator system is added to the polymerization vessel in the course of the free radical aqueous emulsion main polymerization described is of 45 fairly minor importance. The initiator system may be either completely initially taken in the polymerization vessel or added continuously or stepwise at the rate at which it is consumed in

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the course of the free radical aqueous emulsion polymerization. This depends specifically both on the chemical nature of the initiator system and on the polymerization temperature, in a manner known per se to a person skilled in the art.

5

A direct consequence of the abovementioned fact is that the total range from 0 to 100°C is suitable as a reaction temperature for the abovementioned free radical aqueous emulsion main polymerization, but temperatures from 70 to 100°C, preferably from 80 to 100°C, particularly preferably from > 85 to 100°C, are preferably used.

It is possible to use superatmospheric or reduced pressure, so that the polymerization temperature may also exceed 100°C and may be up to 130°C or more. Readily volatile monomers, such as ethylene, butadiene or vinyl chloride, are preferably polymerized under superatmospheric pressure. It is of course possible concomitantly to use molecular weight regulators, such as tert-dodecyl mercaptan, or the novel reducing agents in the free radical aqueous emulsion main polymerization.

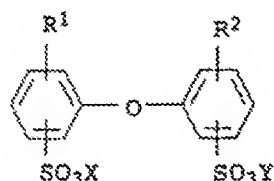
Dispersants are usually present in the free radical aqueous emulsion polymerization and ensure the stability of the aqueous polymer dispersion produced. Suitable dispersants are both the protective colloids usually used for carrying out free radical aqueous emulsion polymerizations and emulsifiers.

Examples of suitable protective colloids are polyvinyl alcohols, cellulose derivatives and vinylpyrrolidone-containing copolymers. A detailed description of further suitable protective colloids appears in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe, Georg-Thieme-Verlag, Stuttgart, 1961, pages 411 to 420. Mixtures of emulsifiers and/or protective colloids can of course also be used. The dispersants used are preferably exclusively emulsifiers whose relative molecular weights, in contrast to the protective colloids, are usually below 1000. They may be anionic, cationic or nonionic. Where mixtures of surfactants are used, the individual components must of course be compatible with one another which, in case of doubt, can be checked on the basis of a few preliminary experiments. In general, anionic emulsifiers are compatible with one another and with nonionic emulsifiers. The same also applies to cationic emulsifiers, whereas anionic and cationic emulsifiers are generally incompatible with one another. Conventional emulsifiers are, for example, ethoxylated mono-, di- and trialkylphenols (degree of ethoxylation: from 3 to 100, alkyl radical: C<sub>4</sub> to C<sub>12</sub>), ethoxylated fatty alcohols (degree of

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ethoxylation: from 3 to 100, alkyl radical: C<sub>8</sub> to C<sub>18</sub>), and alkali metal and ammonium salts of alkyl sulfates (alkyl radical: C<sub>8</sub> to C<sub>18</sub>), of sulfuric half-esters of ethoxylated alkanols (degree of ethoxylation: from 1 to 70, alkyl radical: C<sub>12</sub> to C<sub>18</sub>) and  
 5 ethoxylated alkylphenols (degree of ethoxylation: from 3 to 100, alkyl radical: C<sub>4</sub> to C<sub>12</sub>), of alkanesulfonic acids (alkyl radical: C<sub>12</sub> to C<sub>18</sub>) and of alkylarylsulfonic acids (alkyl radical: C<sub>8</sub> to C<sub>18</sub>). Further suitable emulsifiers, such as sulfosuccinic esters, are described in Houben-Weyl, Methoden der organischen Chemie,  
 10 Volume XIV/1, Makromolekulare Stoffe, Georg-Thieme Verlag, Stuttgart, 1961, pages 192 to 208. Other surfactants which have proven suitable are compounds of the general formula I

15



(I),

20

where R<sup>1</sup> and R<sup>2</sup> are each hydrogen or C<sub>4</sub>-C<sub>24</sub>-alkyl and are not simultaneously hydrogen, and X and Y may be alkali metal ions and/or ammonium ions. In the formula I, R<sup>1</sup> and R<sup>2</sup> are preferably linear or branched alkyl of 6 to 18, in particular 6, 12 or 16,  
 25 carbon atoms or hydrogen, R<sup>1</sup> and R<sup>2</sup> not both simultaneously being hydrogen. X and Y are each preferably sodium, potassium or ammonium ions, sodium being particularly preferred. Particularly advantageous compounds I are those in which X and Y are each sodium, R<sup>1</sup> is branched alkyl of 12 carbon atoms and R<sup>2</sup> is hydrogen  
 30 or R<sup>1</sup>. Frequently, industrial mixtures which contain from 50 to 90 % by weight of monoalkylated product, for example Dowfax® 2A1 (trade mark of Dow Chemical Company), are used. The compounds I are used as dispersants in the novel process preferably as such and particularly preferably as a mixture with ethoxylated fatty  
 35 alcohols (degree of ethoxylation: from 3 to 50, alkyl radical: C<sub>8</sub> to C<sub>18</sub>). The compounds I are generally known, for example from US-A 4,269,749, and are commercially available.

As a rule, the amount of dispersant used is from 0.5 to 6, preferably from 1 to 3, % by weight, based on the monomers to be subjected to free radical polymerization.

The abovementioned dispersants are of course suitable very generally for stabilizing direct novel products of the process. However,  
 45 ever, said products also comprise aqueous polymer dispersions of self-emulsifying polymers, ie. of polymers which have ionic groups which, owing to the repulsion of charges of the same sign,

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have a stabilizing action. Said products preferably effect anionic stabilization (in particular anionic dispersants).

If the preparation of that aqueous polymer dispersion whose residual monomer content is to be reduced in the manner according to the invention is carried out by the free radical aqueous emulsion polymerization method from monomer compositions comprising monomers having at least one ethylenically unsaturated group, monomer compositions which are particularly important with regard to the novel process are those which comprise at least two monomers which differ from one another and have at least one ethylenically unsaturated group, and in addition contain

15 - from 70 to 99.9 % by weight of esters of acrylic and/or methacrylic acid with alkanols of 1 to 12 carbon atoms and/or styrene,

or

20 - from 70 to 99.9 % by weight of styrene and/or butadiene,

or

25 - from 70 to 99.9 % by weight of vinyl chloride and/or vinylidene chloride.

or

30 - from 40 to 99.9 % by weight of vinyl acetate, vinyl propionate and/or ethylene.

Particularly relevant with regard to the novel process are monomer compositions which comprise:

35 from 0.1 to 5 % by weight of at least one  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid of 3 to 6 carbon atoms and/or the amide thereof (monomers A) and

40 from 70 to 99.9 % by weight of esters of acrylic and/or methacrylic acid with alkanols of 1 to 12 carbon atoms and/or styrene (monomers B),

or

45

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from 0.1 to 5 % by weight of at least one  $\alpha,\beta$ -monoethylenic-ally unsaturated carboxylic acid of 3 to 6 carbon atoms and/or the amide thereof (monomers A) and

5

from 70 to 99.9 % by weight of styrene and/or butadiene (monomers B'),

or

10

from 0.1 to 5 % by weight of at least one  $\alpha,\beta$ -monoethylenic-ally unsaturated carboxylic acid of 3 to 6 carbon atoms and/or the amide thereof (monomers A) and

15

from 70 to 99.9 % by weight of vinyl chloride and/or vinylidene chloride (monomers B''),

or

20

from 0.1 to 5 % by weight of at least one  $\alpha,\beta$ -monoethylenic-ally unsaturated carboxylic acid of 3 to 6 carbon atoms and/or the amide thereof (monomers A) and

25

from 40 to 99.9 % by weight of vinyl acetate, vinyl propionate and/or ethylene (monomers B''').

The novel process is also preferable in the case of free radical aqueous emulsion polymerizations of monomer compositions which comprise:

from 0.1 to 30 % by weight of acrylonitrile (preferably from 0.5 to 15 % by weight) and

35

from 70 to 99.9 % by weight of esters of acrylic and/or methacrylic acid with alkanols of 1 to 12 carbon atoms and/or styrene,

40 or

from 0.1 to 30 % by weight of acrylonitrile (preferably from 0.5 to 15 % by weight) and

45 from 70 to 99.9 % by weight of styrene and/or butadiene,

or

from 0.1 to 40 % by weight of vinyl acetate and/or vinyl propionate and

5

from 60 to 99.9 % by weight of esters of acrylic and/or methacrylic acid with alkanols of 1 to 12 carbon atoms and/or styrene.

10 However, the novel process is very particularly preferable in the case of free radical aqueous emulsion polymerizations of monomer compositions which comprise:

15 from 0.1 to 5 % by weight of at least one  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid of 3 to 6 carbon atoms and/or the amide thereof, in particular acrylic acid,

20 from 0.1 to 30 % by weight of acrylonitrile (preferably from 0.5 to 15 % by weight) and

25 from 69.9 to 99.9 % by weight of esters of acrylic and/or methacrylic acid with alkanols of 1 to 12 carbon atoms and/or styrene

or

30 from 0.1 to 5 % by weight of at least one  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid of 3 to 6 carbon atoms and/or the amide thereof, in particular acrylic acid,

35 from 0.1 to 30 % by weight of acrylonitrile (preferably from 0.5 to 15 % by weight) and

from 69.9 to 99.9 % by weight of styrene and/or butadiene,

or

40 from 0.1 to 5 % by weight of at least one  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid of 3 to 6 carbon atoms and/or the amide thereof, in particular acrylic acid,

45 from 0.1 to 40 % by weight of vinyl acetate and/or vinyl propionate and



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from 59.9 to 99.9 % by weight of esters of acrylic and/or methacrylic acid with alkanols of 1 to 12 carbon atoms and/or styrene.

- 5 The stated monomer compositions are preferably chosen so that the  $T_g$  values of the resulting dispersed polymers are below 50°C, preferably below 25°C, very particularly preferably below 0°C (down to -70°C).
- 10 In the case of aqueous polymer dispersions which contain residual monomers and whose dispersed polymer is produced from monomers having at least one ethylenically unsaturated group by free radical aqueous emulsion polymerization, the amount of residual monomers will as a rule reach or fall below the 1 % by weight limit,
- 15 based on the total aqueous dispersion, in this free radical aqueous emulsion main polymerization itself. Where this is not possible, the novel process for reducing the residual monomer content can, as stated above, either be used directly thereafter, or the conventional prior art methods for reducing residual monomer contents may be used initially until the abovementioned limit
- 20 is reached before continuing according to the invention in order to utilize the advantages of the novel process. In general, the main polymerization reaction and the novel step of the reduction of the residual monomer contents may follow one another smoothly.
- 25 Furthermore, the novel free radical redox initiator system may already have been present in the main polymerization reaction.

In addition to the reducing agents to be used according to the invention, the free radical redox initiators to be used according

30 to the invention may of course also comprise other reducing agents, such as reducing sugars, eg. glucose and fructose, derivatives thereof, such as ascorbic acid, or sulfinic acids, such as hydroxymethanesulfinic acid, or alkanesulfinic acids, such as isopropanesulfinic acid (or salts thereof). Preferably, however,

35 the novel reducing agents account for more than 50, preferably more than 75, % by weight of the total amount of reducing agents used and very particularly preferably are the sole reducing agent.

40 Suitable oxidizing components of the free radical redox initiators to be used according to the invention are, for example, molecular oxygen, ozone, agents which evolve oxygen with formation of free radicals and do not have a peroxide structure, such as alkali metal chlorates and perchlorates, transition metal oxide

45 compounds, such as potassium permanganate, manganese dioxide and lead oxide, as well as lead tetraacetate and iodobenzene. How-

ever, peroxides, hydroperoxides or mixtures thereof are preferably used.

Hydrogen peroxide, in particular in combination with mercapto-  
5 ethanol, peroxodisulfuric acid and its salts, in particular its  
alkali metal salts (ie. Na and K), alkali metal perborates, per-  
oxodiphosphates, tert-butyl hydroperoxide and others have proven  
advantageous. According to the invention, exclusively inorganic  
oxidizing agents are preferably used since, in combination with  
10 the novel reducing agents, this permits subsequent emission-free  
chemical deodorization.

Oxidizing agents and reducing agents should as a rule be used in  
the novel process in a molar ratio of from 1:1 to 5:1. They are  
15 preferably used in roughly equivalent amounts.

In the novel process, the free radical redox initiator system to  
be used according to the invention can in principle be added all  
at once to the aqueous polymer dispersion containing the residual  
20 monomers. However, the oxidizing agent may also be added all at  
once and then the reducing agent fed in continuously. However, it  
is also possible for the oxidizing agent and the reducing agent  
to be added continuously in the course of a few (from 0.5 to 6,  
preferably from 1 to 3) hours, via separate feeds, to the aqueous  
25 polymer dispersion to be treated.

Of course, the amounts of free radical redox initiator system to  
be used according to the invention depend on the amount of resid-  
ual monomers still present and on the desired degree of reduction  
30 of the content of said monomers.

As a rule, the amount to be used is from 0.01 to 5, advanta-  
geously from 0.1 to 1, % by weight, based on the dispersed poly-  
mer or on about 10 times the weight of the residual monomers. It  
35 is of course possible for the novel process to be followed by  
other processes for the reduction of residual monomer contents.

Finally, it should be stated that the free radical redox initia-  
tor systems to be used according to the invention permit an ef-  
40 fective reduction of the residual monomer content in a short  
time. The residual monomer contents determined in the examples  
below are based on gas chromatographic determinations.

It should furthermore be stated that the use of the reducing  
45 agents to be employed according to the invention, in combination  
with inorganic oxidizing agents, gives rise to virtually no vola-

## 23

tile organic secondary products. This is also shown in the examples below.

In the test for volatile organic secondary products, 1 g of a solution of 300 mg of dioxane (standard) in one kg of water was added to 1 g of each aqueous polymer dispersion treated according to the invention. Thereafter, 5  $\mu$ l of the aqueous polymer dispersion diluted in this manner were introduced into a tightly sealable container having an internal volume of 22 ml and kept in the closed container for 15 minutes at 150°C. The gas phase of the interior of the container was then analyzed by gas chromatography. This was carried out by means of a fused silica capillary column DB-1 of medium polarity, from J & W Scientific Folsom, USA. In all examples according to the invention, the content of volatile organic secondary products was below the limit of detection of 5 ppm (parts by weight, based on the dispersion).

## Examples

- 20 a) An aqueous polymer dispersion which was stabilized with 0.1 % by weight of Dowfax 2A1 and 0.1 % by weight of sodium lauryl sulfate (the stated amount in each case is based on polymer) and had a number average polymer particle diameter of 150 nm and whose solids content was 50 % by weight was produced from a monomer mixture having the composition

50 % by weight of n-butyl acrylate,  
46 % by weight of styrene,  
2 % by weight of acrylic acid and  
30 2 % by weight of methacrylic acid

with the use of sodium peroxodisulfate by the monomer emulsion feed procedure at a polymerization temperature of 80°C.

- 35 Gas chromatographic analysis of the aqueous polymer dispersion gave a residual monomer content of 7000 ppm (weight, based on dispersion) of n-butyl acrylate.

- After the pH of the aqueous dispersing medium of the aqueous polymer dispersion had been brought to 7,

3·10<sup>-2</sup> mol of H<sub>2</sub>O<sub>2</sub>, dissolved in 30 ml of water, and  
1·10<sup>-2</sup> mol of reducing agent, dissolved in 30 ml of  
water,

45

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were added continuously in the course of 3 hours, beginning at the same time, to 1 kg of each aqueous polymer dispersion at 60°C in separate feeds.

5 The aqueous polymer dispersion was then investigated by gas chromatography to determine the remaining content of free n-butyl acrylate and to determine volatile organic secondary products (including the reducing agent used). The results obtained are shown in Table 1 below, as a function of the re-  
10 ducing agent used. Table 1 additionally shows the result when H<sub>2</sub>O<sub>2</sub> is used alone and when the reducing agent is used alone.

Table 1

Reducing agent	Residual n-butyl acrylate content (ppm)	Volatile organic secondary products
3-Mercaptopropionic acid	261	-
20 2-Mercaptopropionic acid	619	-
Thioacetic acid	236	-
Thiomalic acid	57	-
L-Cysteine	199	-
25 Sodium 2-mercaptoethanesulfonate	307	-
-(H <sub>2</sub> O <sub>2</sub> alone)	2624	-
2-Mercaptopropionic acid (without H <sub>2</sub> O <sub>2</sub> )	5055	Mercaptopropionic acid
30 Ascorbic acid	752	not investigated
Sodium metabisulfite	2449	-
Rongalit	2311	Formaldehyde

35 b) A 50 % strength by weight aqueous polymer dispersion whose number average particle diameter was 170 nm and which had a residual styrene monomer content of 2500 ppm, determined by gas chromatography, was produced in a manner similar to that  
40 described under a), from a monomer mixture having the composition

60 % by weight of styrene,  
38 % by weight of butadiene and  
45 2.0 % by weight of acrylic acid

## 25

(initiated by sodium peroxodisulfate and stabilized by means of 0.8 % by weight of sodium laurylsulfate (based on polymer)).

- 5 The procedure described under a) was used for reducing the residual monomer content. However, the feeds consisted of

1.10<sup>-2</sup> mol of H<sub>2</sub>O<sub>2</sub>, dissolved in 30 ml of water, and  
1.10<sup>-2</sup> mol of reducing agent in 30 ml of water.

10

The results are shown in Table 2 below.

Table 2

15

Reducing agent	Residual styrene content (ppm)	Volatile secondary products
3-Mercaptopropionic acid	670	-
Sodium metabisulfite	1963	-
Rongalit	904	Formaldehyde
Ascorbic acid	770	not investigated

20

- c) As a comparative experiment, the procedure described in b) was followed, but the feeds consisted of

1.10<sup>-2</sup> mol of H<sub>2</sub>O<sub>2</sub>, dissolved in 30 ml of water, and  
1.10<sup>-2</sup> mol of tert-dodecyl mercaptan, emulsified in  
30 ml of water.

30

The resulting residual styrene content was 1938 ppm.

Owing to the absence of volatile organic secondary products, no subsequent deodorization of the resulting aqueous polymer dispersion to eliminate these volatile secondary products is required when the novel process is used.

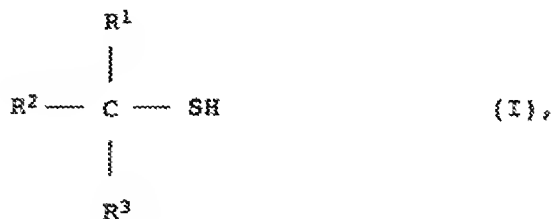
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We claim:

1. A process for the preparation of an aqueous polymer dispersion, in which an aqueous dispersion of a polymer which contains at least one monomer, having at least one ethylenically unsaturated group, incorporated in chemically bonded form is produced in a manner known per se, so that the total content, based on the polymer content of the aqueous polymer dispersion, of monomers which are free, is not chemically bonded, and have at least one ethylenically unsaturated double bond is from  $> 0$  to  $\leq 1$  % by weight, and this residual monomer content is then reduced by the action of a free radical redox initiator system comprising at least one oxidizing agent and at least one reducing agent, wherein the redox initiator system contains, as reducing agent, at least one mercaptan which, in addition to the thiol group, has at least one further functional group which comprises at least one atom other than hydrogen and carbon and whose electronegativity is above that of the hydrogen atom, with the exclusion of those processes in which the total amount of mercaptan is added completely to the aqueous polymer dispersions containing the residual monomers before the addition of the oxidative component of the free radical redox initiator system.
2. A process as claimed in claim 1, wherein the residual monomer content to be reduced is from  $> 0$  to  $\leq 0.5$  % by weight.
3. A process as claimed in claim 1, wherein the residual monomer content to be reduced is from  $> 0$  to  $\leq 0.1$  % by weight.
4. A process as claimed in claim 1, wherein the mercaptan is a mercaptan selected from the group consisting of thiocarboxylic acids of 1 to 8 carbon atoms and the alkali metal and ammonium salts thereof and the members which differ from thiocarboxylic acids of 1 to 8 carbon atoms and are of the formula I



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where  $R^1$ ,  $R^2$ ,  $R^3$ , independently of one another, are each hydrogen, one of the following functional groups  $-OR^4$  where  $R^4$  is hydrogen or  $C_1$ - $C_4$ -alkyl,  $-NHR^4$ ,  $-COOR^4$ ,  $-SO_2R^4$ ,  $-SO_3R^4$ ,  $-OSO_3R^4$ ,  $-SR^4$ ,  $-NO_2$ ,  $-CN$ ,  $-SCN$ ,  $-halide$ ,  $-COSR^4$ ,  $-CSOR^4$ ,  $-COR^4$ ,  $-CSR^4$ ,  $-CSSR^4$ ,  $-CSNHR^4$ ,  $-CONHR^4$ ,  $-COOhalide$ ,  $-CSShalide$  where halide is F, Cl, Br or I,  $-OPO_3HR^4$ ,  $-PO_3HR^4$  and  $-OPO_3R^4$ , the alkali metal and ammonium salt thereof also being suitable in the case of acidic functional groups, a phenyl radical, a benzyl radical or an alkyl radical of 1 to 8 carbon atoms, where one or two hydrogen atoms of each of these radicals may be replaced by one of the above functional groups and where two of the unsubstituted or substituted alkyl radicals may furthermore form a saturated ring having 5 or 6 carbon atoms, with the proviso that the mercaptans I have at least one and not more than three of the abovementioned functional groups in addition to the thiol group, and at least one of the radicals  $R^1$ ,  $R^2$  and  $R^3$  is an unsubstituted or substituted phenyl or benzyl radical or an unsubstituted or substituted alkyl radical of 1 to 8 carbon atoms, as described above.

5. A process as claimed in any of claims 1 to 4, wherein the mercaptan is one selected from the group consisting of mercaptoacetic acid, 3-mercaptopropionic acid, 2-mercaptopropionic acid, thioacetic acid, thiomalic acid, L-cysteine, mercaptoethanol, sodium 3-mercaptopropanesulfonate and sodium 2-mercaptoethanesulfonate.
6. A process as claimed in any of claims 1 to 5, wherein the solids volume content of the aqueous polymer dispersion produced in a manner known per se is from 30 to 70 % by volume.
7. A process as claimed in any of claims 1 to 6, wherein the redox initiator system acts at a pH of the aqueous dispersing medium of from 6 to 10.
8. A process as claimed in any of claims 1 to 7, wherein the dispersed polymer of the aqueous polymer dispersion produced in a manner known per se is prepared from monomers having at least one ethylenically unsaturated group by the free radical aqueous emulsion polymerization method.
9. A process as claimed in claim 8, wherein the monomer composition to be polymerized for the preparation of the dispersed polymer comprises at least two monomers which differ from one another and have at least one ethylenically unsaturated group, and in addition contains



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- from 70 to 99.9 % by weight of esters of acrylic or methacrylic acid with alkanols of 1 to 12 carbon atoms or styrene,

5 or

- from 70 to 99.9 % by weight of styrene or butadiene,

or

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- from 70 to 99.9 % by weight of vinyl chloride or vinylidene chloride,

or

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- from 40 to 99.9 % by weight of vinyl acetate, vinyl propionate or ethylene.

10. A process as claimed in any of claims 1 to 9, wherein the  
20 free radical redox initiator system comprises exclusively inorganic oxidizing agents.

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